

ACCEPTED MANUSCRIPT • OPEN ACCESS

The path towards 1 μm monocrystalline Zn_3P_2 films on InP : substrate preparation, growth conditions and luminescence properties

To cite this article before publication: Mahdi Zamani *et al* 2021 *J. Phys. Energy* in press <https://doi.org/10.1088/2515-7655/abf723>

Manuscript version: Accepted Manuscript

Accepted Manuscript is "the version of the article accepted for publication including all changes made as a result of the peer review process, and which may also include the addition to the article by IOP Publishing of a header, an article ID, a cover sheet and/or an 'Accepted Manuscript' watermark, but excluding any other editing, typesetting or other changes made by IOP Publishing and/or its licensors"

This Accepted Manuscript is © 2021 The Author(s). Published by IOP Publishing Ltd.

As the Version of Record of this article is going to be / has been published on a gold open access basis under a CC BY 3.0 licence, this Accepted Manuscript is available for reuse under a CC BY 3.0 licence immediately.

Everyone is permitted to use all or part of the original content in this article, provided that they adhere to all the terms of the licence <https://creativecommons.org/licenses/by/3.0>

Although reasonable endeavours have been taken to obtain all necessary permissions from third parties to include their copyrighted content within this article, their full citation and copyright line may not be present in this Accepted Manuscript version. Before using any content from this article, please refer to the Version of Record on IOPscience once published for full citation and copyright details, as permissions may be required. All third party content is fully copyright protected and is not published on a gold open access basis under a CC BY licence, unless that is specifically stated in the figure caption in the Version of Record.

View the [article online](#) for updates and enhancements.

The path towards 1 μm monocrystalline Zn₃P₂ films on InP: substrate preparation, growth conditions and luminescence properties

Mahdi Zamani ¹, Elias Stutz ¹, Simon Escobar ¹, Reza Zamani ², Rajrupa Paul ¹, Jean-Baptiste Leran ¹, Mirjana Dimitrievska ¹, Anna Fontcuberta i Morral ^{1,3,*}

¹ Laboratory of Semiconductor Materials, Institute of Materials, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

² Centre Interdisciplinaire de Microscopie Électronique, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

³ Institute of Physics, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

* corresponding author : anna.fontcuberta-morral@epfl.ch

Abstract

Semiconductors made with earth abundant elements are promising as absorbers in future large-scale deployment of photovoltaic technology. This paper reports on the epitaxial synthesis of monocrystalline zinc phosphide (Zn₃P₂) films using molecular beam epitaxy (MBE) with thicknesses up to 1 μm thickness on InP (100) substrates, as demonstrated by high resolution transmission electron microscopy and X-ray diffraction. We explain the mechanisms by which thick monocrystalline layers can form. We correlate the crystalline quality with the optical properties by photoluminescence at 12 K. Polycrystalline and monocrystalline films exhibit dissimilar photoluminescence below the bandgap at 1.37 and 1.30 eV, respectively. Band edge luminescence at 1.5 eV is only detected for monocrystalline samples. This work establishes a reliable method for fabricating high-quality Zn₃P₂ thin films that can be employed in next generation photovoltaic applications.

Keywords: Zn₃P₂, thin films, earth-abundant semiconductors, photovoltaics

Introduction

The adverse impact of global energy consumption on the environment necessitates a massive shift in energy production toward more sustainable and non-fossil energy sources. A prominent part of a multicomponent solution is the large-scale deployment of photovoltaic (PV) energy production, which can be facilitated using semiconductors made of earth-abundant elements (1–3). However, many earth-abundant semiconductors suffer from narrow growth windows, thermodynamic instability, coexistence of multiple phases and long term degradation among other factors (4–8), affecting the performance of PV devices. A common challenge with many of these materials is the inclusion of a cation with multiple oxidation states, which, especially in high oxidation states, is likely to switch to lower oxidation numbers (9). α -Zn₃P₂, on the other hand, is a candidate material with promising advantages, such as the simplicity of Zn–P system phase diagram (10–12) and thermodynamic stability thanks to the singular oxidation state of zinc. It demonstrates high absorption of more than 10⁴ cm^{−1} in the visible range of the

electromagnetic spectrum (13,14), reported bandgap close to the optimal value of the Shockley–Queisser limit (12,15), carrier diffusion length in the range of 5–10 μm (16) and passive grain boundaries (17), which in turn could improve the performance of PV devices based on this material

Epitaxial growth of high-quality Zn₃P₂ is inherently difficult, in part because of its very large tetragonal unit cell (18), with $a = 8.089 \text{ \AA}$ and $c = 11.45 \text{ \AA}$ (19), making it challenging to find commercially available substrate for epitaxial growth. Zn₃P₂ tends to grow in the (001) direction (20). In this orientation, the P sub-lattice of the tetragonal unit cell exhibits a low lattice mismatch with the group V elements of (001) oriented InP and GaAs (2.4% and 1.3% respectively). Still, monocrystalline layers have been limited to a thickness of 150 nm on GaAs (100) (17). The other difficulty in the growth of high-quality Zn₃P₂ thin films stems from its high thermal expansion coefficient. For instance, this coefficient is $14 \times 10^{-6} \text{ K}^{-1}$ at room temperature for Zn₃P₂ (21) in comparison to $6 \times 10^{-6} \text{ K}^{-1}$ and $3 \times 10^{-6} \text{ K}^{-1}$ for GaAs and Si,

respectively. Upon cooling down, the mismatch in coefficient of thermal expansion results in formation of cracks in the thin films grown at high temperatures (22). A recent solution that overcome these challenges corresponds to growth on graphene substrates by van der Waals epitaxy (23). In addition, restricting the interface with the substrate to nanoscale regions via the creation of nanowires or selective area epitaxy are also being investigated as potential solutions (23–26). To the best of our knowledge, to date none of these strategies has yet provided large area monocrystalline structures.

In this work, we report on the growth requirements to achieve monocrystalline Zn_3P_2 thin films on $\text{InP}(100)$ substrates using molecular beam epitaxy (MBE). Growth parameters such as substrate temperature, ratio between P and Zn fluxes (V/II ratio) and substrate preparation are varied, resulting in amorphous, polycrystalline and monocrystalline thin films. A range of characterization techniques including Raman spectroscopy, X-ray diffraction (XRD), (scanning) transmission electron microscopy (S/TEM) and electron energy loss spectroscopy (EELS) have been employed to shed light on the differences between thin films obtained in different conditions. As a key parameter, we find that substrate surface preparation by effectively removing the native oxide is essential for obtaining monocrystalline layers. Finally, the optical properties of the thin films are investigated using photoluminescence (PL) spectroscopy and the differences between the characteristics of polycrystalline and monocrystalline Zn_3P_2 thin films are demonstrated.

Results and Discussion

We start by exploring the role of the V/II ratio calibrated using a beam flux monitor and the manipulator temperature on the crystalline quality of the thin films. Substrate preparation includes two steps of sample degassing for two hours each at 150°C and 300°C in ultra-high vacuum, and a third step under P_2 flux $> 1 \times 10^{-6}$ torr at a manipulator temperature of 580°C to fully remove surface contaminants and the native oxide. The effects of duration of the last annealing step are discussed further down. Figure 1(a) and 1(b) depict cross-sectional scanning electron microscopy (SEM) images of typical amorphous and polycrystalline thin films, grown with $V/II = 0.83$, $T = 280^\circ\text{C}$ and $V/II = 0.48$, $T = 265^\circ\text{C}$, respectively. The thin film in Fig. 1(a) shows a continuous and smooth structure, while in Fig. 1(b) one finds a granular structure, denoting the polycrystalline nature of the film. In this case, the cross-section SEM indicates that growth starts by forming small grains that gradually merge into larger grains as growth continues. Room temperature Raman measurements have been conducted on the samples to assess their crystalline

quality. Figure 1(c) displays the Raman spectra for thin films grown with V/II ratios between 0.43 and 1.37 and substrate temperatures between 250°C and 290°C . The characteristic spectrum of $\alpha\text{-Zn}_3\text{P}_2$ is observed (27). A dozen low-wavenumber peaks, dominated by Zn atom displacements, merge into the broad peak at approximately 93 cm^{-1} , while the high-wavenumber peaks, mainly dominated by P atom displacements, merge into a series of overlapping peaks in the range from 280 cm^{-1} to 360 cm^{-1} (27). The spectra of thin films grown at high V/II ratios (1.35 and 0.95) are mainly featureless or with few broad peaks, suggesting that samples obtained at high V/II ratios are amorphous, as reported in (26). This is also the case for thin films obtained at the highest temperature, 280°C . For V/II ratios between 0.72 and 0.95 Raman spectra of thin films grown at 250°C and 265°C are consistent with crystallinity. Similar trends have been recently observed for growth of Zn_3P_2 on graphene (26).

To further improve the crystalline quality and reproducibility, effects of the third degassing step at 580°C for different durations are investigated. Figure 2 shows representative SEM cross-section micrographs of thin films obtained for increased degassing durations, namely 10, 20, 30, 45, 60 and 75 min. We observe that for the identical growth conditions, increasing the degassing time renders the thin films less granular. In fact, the granular nature disappears for annealing periods of 30 min or higher. Raman studies indicate that these samples are crystalline. In addition, the top surfaces of the thin films get smoother. It is to be noted that while increasing this degassing time makes it possible to obtain monocrystalline samples in a reproducible manner, a few samples with degassing times of 10 min were also monocrystalline, as presented in Figure 3. However, the occurrence of the monocrystallinity tends to be non-reproducible for samples with degassing times less than 20 min. In Figure 2(g), we show representative Raman spectra of a monocrystalline and a polycrystalline thin film acquired at 12 K with an incidence wavelength of 532 nm. A lower material temperature increases the phonon lifetime. This decreases the uncertainty of the phonon energy, lowering peak width and thus the overlap between the multiple peaks. We find that the Raman spectra obtained in different spots on each sample consistent, indicating relatively homogeneous crystalline quality. However, changes in relative intensities of the peaks can be observed between the two samples. We attribute these differences to changes in the concentrations of point defects such as interstitials/vacancies or grain boundaries, which affect different vibrational modes of the lattice in varying ways. A detailed study to identify the defects in Zn_3P_2 thin films with Raman spectroscopy is ongoing.

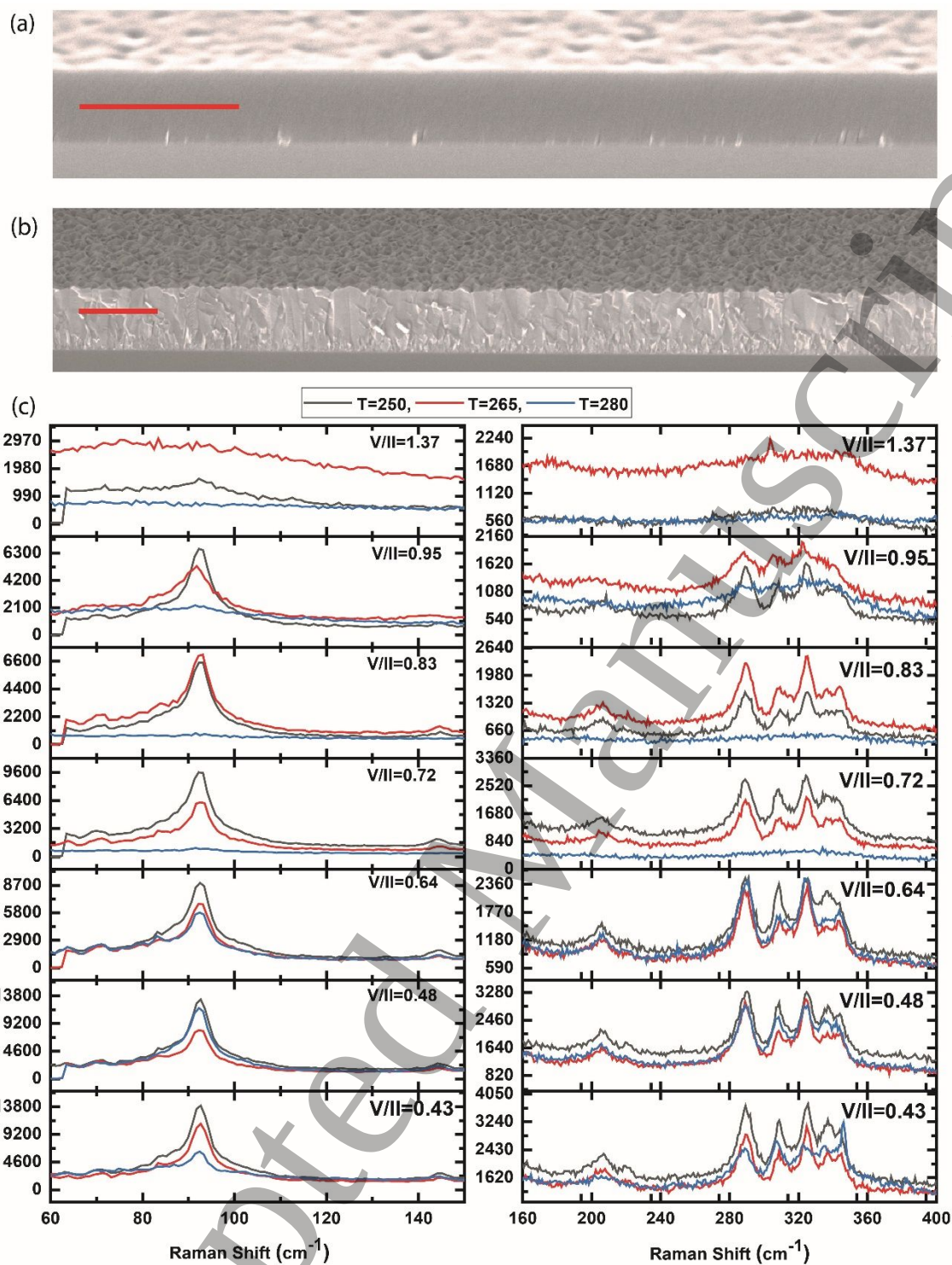


Figure 1: effect of growth temperature and V/II ratios. (a): 20° tilted cross section image of an amorphous Zn_3P_2 thin film grown with $V/II = 0.83$ and $T = 280^\circ C$. (b): tilted cross section image of a polycrystalline Zn_3P_2 thin film grown with $V/II = 0.48$ and $T = 265^\circ C$, demonstrating the presence of grain boundaries. Scale bars are $1\mu m$. (c) Micro-Raman with 532 nm laser for samples grown at different growth temperatures and V/II ratios. Increasing the growth temperature and V/II ratio makes the films amorphous. All the samples reported in this figure have degassing time at $580^\circ C$ of 10 mins and P flux of 4.3×10^{-7} torr.

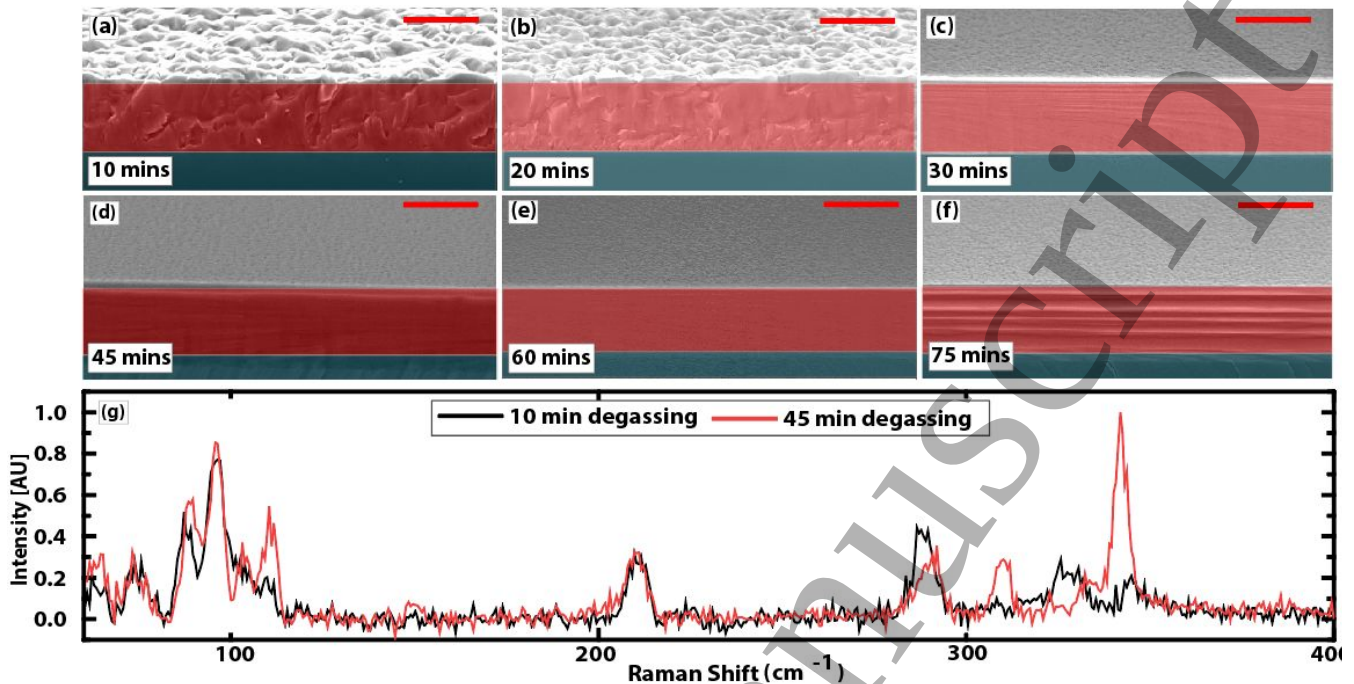


Figure 2: (a) – (f) SEM images demonstrating the effects of degassing time at 580 °C on the crystalline quality of Zn_3P_2 thin films. No apparent grains are observed for a degassing time ≥ 30 mins. The red scale bar is 1 μm . The transparent blue layer indicated the substrate, while the transparent red area highlights the cross section of the thin films. (g) comparison of the Raman spectra of samples with degassing time at 580 °C of 10 min and 45 min. These samples are polycrystalline and monocrystalline, respectively. All the samples reported here are grown on on p-doped $InP(100)$ substrates with identical growth conditions of $T = 245^\circ C$, $V/II = 0.72$ and $P = 5.81 \times 10^{-7} torr$. The SEM images are acquired at 20° tilt.

High-resolution (HR) TEM and aberration-corrected high-angle annular dark-field (HAADF) STEM are used to investigate the crystalline quality. Figure 3(a) corresponds to a HRTEM image of a thin film obtained with $V/II = 0.72$, $T = 265^\circ C$ and the degassing time of 10 min at 580 °C. HRTEM indicates that this is a monocrystalline thin film. The diffraction pattern obtained on a larger area also corroborates the monocrystallinity, as shown in the inset of Figure 3(a). Calculations of atomic distances based on the selective-area diffraction pattern demonstrates a lattice mismatch of 2% considering the pseudo-cubic structure of Zn_3P_2 and the growth direction of [001], consistent with previous studies (20,25). The HAADF-STEM image of this sample in Figure 3(b) adds further details of the interface between the film and the substrate. Considering that the heavier atoms appear brighter in HAADF-STEM images due to Z-contrast (28–30), the constituting elements can be assigned across the interface. The brightness of atoms at the interface, intermediate between the one observed for In in the substrate and Zn in the layer indicates the formation of a mixed $Zn-In$ monolayer, as depicted in the blue inset of figure 3(b). The monolayer Zn-In

intermixing establishes the epitaxial transition from the InP substrate to the Zn_3P_2 film. The red inset of this figure establishes that while monocrystalline, these films may still include some structural defects stemming from misalignment of the systematic vacant sites in c direction. Figure 3(c) probes the oxygen core-loss EELS signature at 532 eV across the interface of this sample, demonstrating a uniform absence of oxygen around this area. Figure 3(d) corresponds to a low magnification TEM image of a sample obtained at $V/II = 0.48$, $T = 265^\circ C$ and with a degassing time of 10 min at 580 °C. The micrograph shows the polycrystalline nature with a clear pattern of columnar-structured grains. The HAADF-STEM image of this sample in Figure 3(e) further highlights the difference between the polycrystalline and the monocrystalline thin films, as the area above the interface appears diffused as opposed to the sharp interface of the monocrystalline film. Moreover, in this micrograph one can notice the randomly oriented atomic fringes in the thin film. Figure 3(f) corresponds to the oxygen map by core-loss EELS of the interface area shown in Figure 3(e). There is a clear oxygen signature at the interface. The presence of an oxide

could be the reason for the lack of sharpness of the interface in the HAADF image. In summary, the increase in degassing time at 580 °C promotes the complete desorption of the

substrate native oxide in a consistent manner, which in turn facilitates the formation of a monocrystalline thin film.

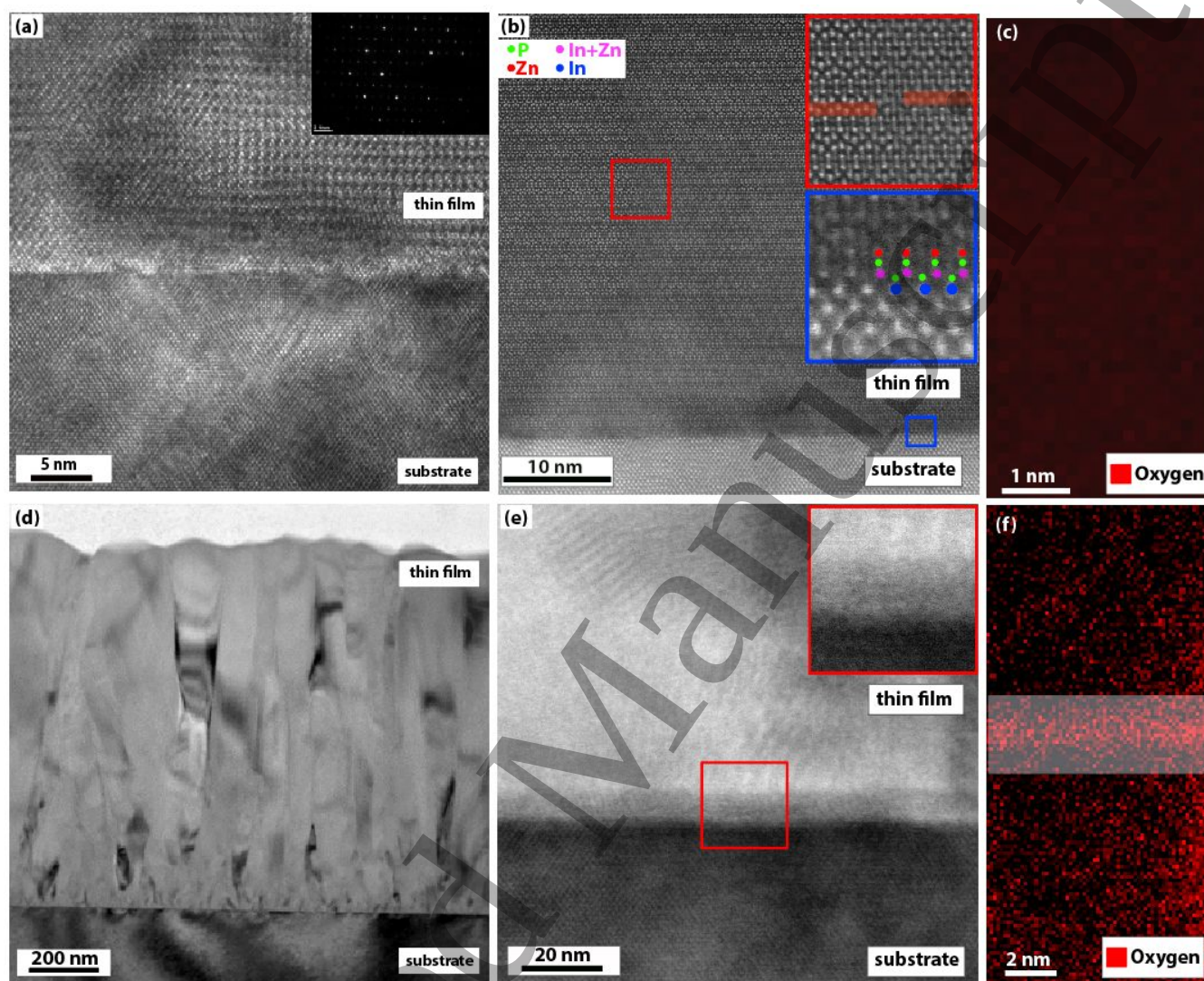


Figure 3: (S)TEM/ EELS comparison of monocrystalline and polycrystalline thin films. (a) HRTEM image of a monocrystalline sample grown at $V/II = 0.72$, $T = 265\text{ }^{\circ}\text{C}$ and with a degassing time of 10 min at 580 °C. The inset depicts a diffraction pattern corresponding to a larger area. (b) HAADF-STEM image of the same sample showing the epitaxial relationship between the substrate and the thin film. The blue inset demonstrates the state of interface while the red inset highlights in-plane defect stemming from the vertical misalignment of the systematic vacant sites. (c) The core-loss oxygen EELS map of the interface between the substrate and the monocrystalline thin film demonstrating the absence of oxygen across the interface. (d) low-magnification TEM image of a polycrystalline sample grown at $V/II = 0.48$, $T = 265\text{ }^{\circ}\text{C}$ and the degassing time of 10 min at 580 °C. (e) HAADF-STEM image of the same sample showing the diffused interface and the lack of epitaxial relationship between the substrate and the polycrystalline thin film. (f) The core-loss oxygen EELS map of the interface between the substrate and the polycrystalline thin film demonstrating the pronounced concentration of oxygen across the interface highlighted by the transparent white strip overlaying the map.

To further examine the crystalline quality of the thin films obtained under the different conditions, high resolution XRD was performed. Figure 4 compares the XRD pattern for bare

InP substrate, amorphous, polycrystalline and monocrystalline Zn_3P_2 thin films. The growth conditions of each thin film are presented in the figure caption. The most

intense peak, observed at 30.4° , corresponds to the (200) reflection of the *InP* substrate (31). Dashed vertical lines are employed to highlight the location of the peaks stemming from the *InP* substrate. Some of these peaks are absent on the amorphous sample (with broad peaks of Zn_3P_2 in the Raman spectra). The main crystalline signature of Zn_3P_2 , observed at 31.4° corresponds to the (004) reflection (32), and is observed on both polycrystalline and monocrystalline thin films. Multiple peaks corresponding to the higher index planes are observed for the polycrystalline thin film between 30° and 50° . These peaks are absent on the monocrystalline film, with only peaks corresponding to (002), (004) and (006) directions of Zn_3P_2 being visible. This indicates that the growth direction of the monocrystalline film is [001], consistent with the HRTEM analysis.

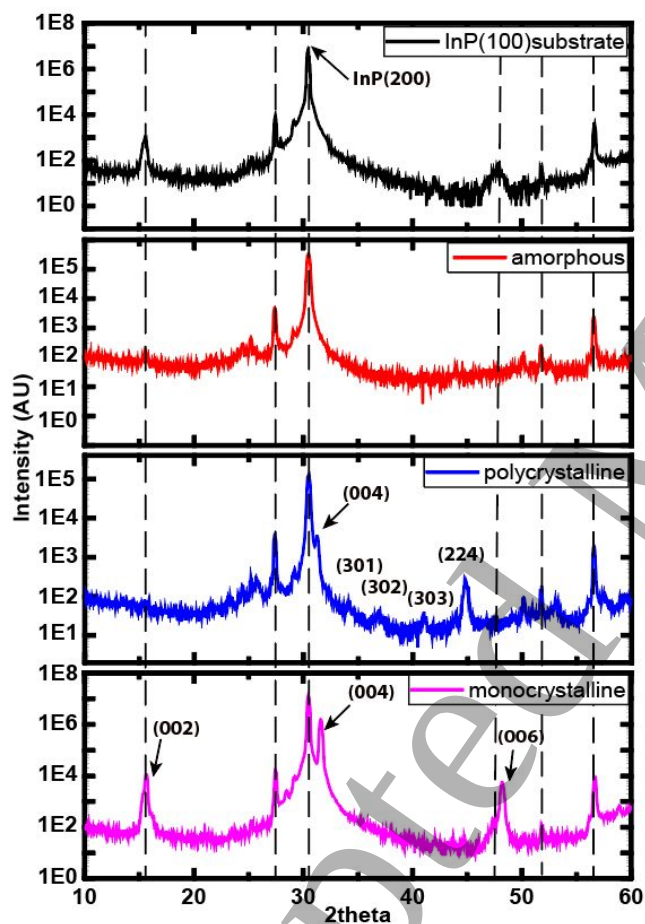


Figure 4: XRD comparison of different sample types. (a) XRD scan of a bare *InP*(100) substrate showing a pattern dominated by (200) peak at 30.4° and few other *InP* peaks. The dashed black lines indicate the position of *InP* substrate peaks which are also observed on the other samples. (b) XRD pattern of an amorphous sample with $V/II = 0.83$ and $T = 280^\circ\text{C}$ (c) XRD pattern of a polycrystalline sample grown at $V/II = 0.48$, $T = 265^\circ\text{C}$ and with a degassing time of 10 min at 580°C , demonstrating the Zn_3P_2 (004) peak at 31.4°

in addition to other, less intense peaks between 30° and 50° that correspond to higher-index planes. (d) XRD pattern of a monocrystalline sample grown at $V/II = 0.72$, $T = 265^\circ\text{C}$ and with a degassing time of 10 min at 580°C . From Zn_3P_2 , only (002), (004) and (006) peaks are observed, which all belong to the {001} family.

Low temperature PL was performed to evaluate and compare the optical properties of the polycrystalline and monocrystalline samples. In general, we find that the emission spectrum from polycrystalline samples strongly depends on the growth parameters. In Figure 5, representative PL measurements for one polycrystalline and one representative monocrystalline sample measured with an excitation are shown. In addition, the 20 K wavelength of 488 nm at substrate is also included as *InP* emission spectrum of a bare a reference. The orange curve in Figure 5 corresponds to the PL data of a typical polycrystalline sample. The emission thin films consists of a P_2n_3Z spectra from polycrystalline single peak or a single set of overlapping peaks at energies lower than the direct bandgap energy (15,33). The low-energy emission was not expected to be so much stronger than the higher band-to-band-like transitions, based on previous reports (15). Further work is ongoing to understand and quantify the different types of emission. Similar results have and in other systems in the past and P_2n_3Z been observed in are attributed to defects (34,35). Other polycrystalline films, not shown in this figure, emit at slightly different energies, generally within a few dozen meV below 1.4 eV. The substrate emission is almost always observed, even though the film thickness is several times the penetration depth of the laser (15). This could be due the much larger radiative Z substrate compared to *InP* recombination efficiency of the thin films or the diffusion of carriers from the film to the P_2n_3Z substrate. In addition to the differences in the optical properties of the different polycrystalline films, their emission shows minor variation based on the location, which could be due to the local variation of the properties such as density of defects across the thin film. If the probability of recombining through a radiative path instead of a non-radiative path is different in the substrate and the film, any change in the diffusion and trapping of carriers may affect the relative intensities of the substrate and film emissions.

Our monocrystalline thin films exhibit a homogeneous emission spectrum over the whole sample. In Figure 5, a representative photoluminescence spectrum of a monocrystalline sample is demonstrated by the black curve. The *InP* substrate emission is still measurable at 1.43 eV. For Zn_3P_2 we observe two peaks: a broad peak at lower energy, 1.3 eV and another at higher-energy centered around 1.52 eV. The latter is consistent with the direct bandgap of Zn_3P_2 (15).

The inset in Figure 5 illustrates a magnified view of this peak. Although Kimball *et al.* attributed the 1.3 eV emission to the indirect bandgap (15), we find it difficult to justify a higher emission intensity for an indirect transition. We think this emission may rather be linked to radiative recombination from

defect levels below the bandgap. On the other hand, Briones *et al.* assigned the transitions observed in their spectra in the range of 1.31 eV to 1.37 eV to donor-acceptor pair transitions (36).

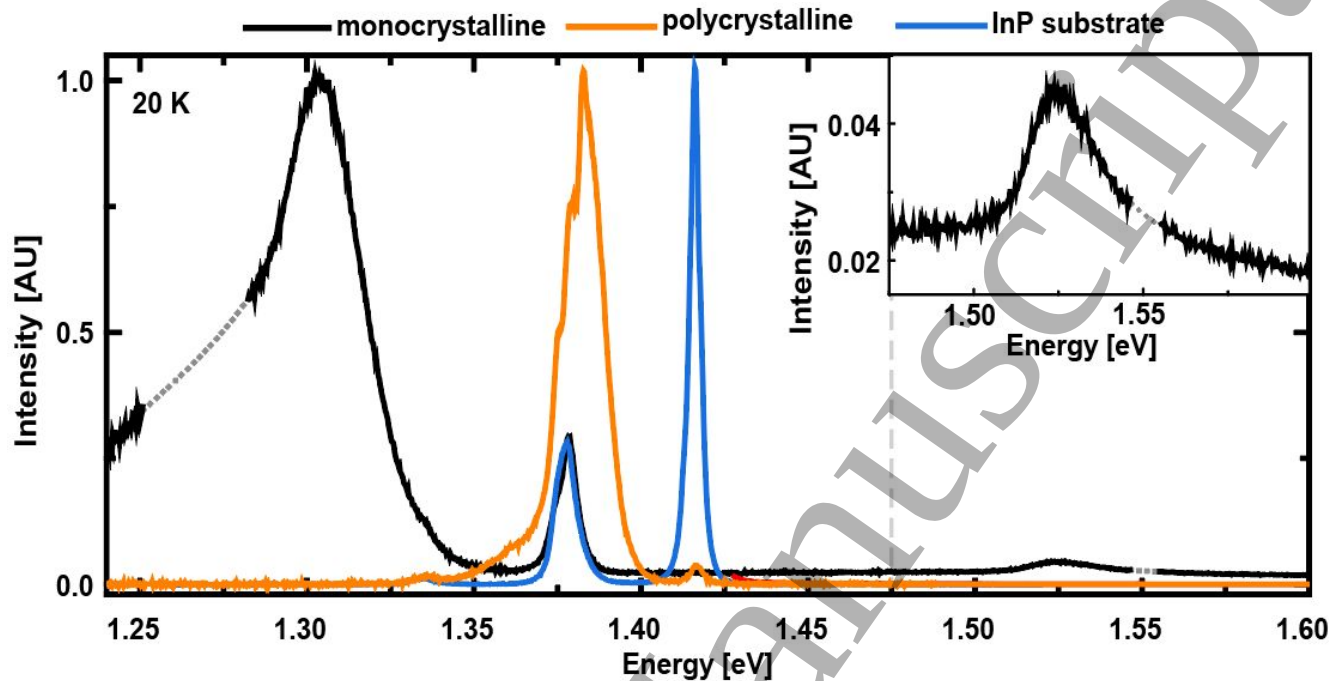


Figure 5: Photoluminescence measurements showing the difference in the optical properties of polycrystalline and monocrystalline samples. The dashed parts of the curves are where the laser peaks have been removed for the spectra of the monocrystalline sample. The measurements have been conducted at 20 K using radiant fluxes of $470 \mu W$, $0.47 \mu W$ and $1170 \mu W$ on the monocrystalline, polycrystalline and *InP* substrate samples, respectively. $V/II = 0.72$, $T = 265^\circ C$ and $V/II = 0.48$, $T = 265^\circ$ have been used to grow the monocrystalline and polycrystalline samples, respectively, with a degassing time of 10 min at $580^\circ C$ for both. The thicknesses of monocrystalline and polycrystalline films are ~ 800 nm and 750 nm, respectively.

Conclusion

In this study, we provide the main elements for the growth of monocrystalline Zn_3P_2 films with thicknesses up to $1 \mu m$ over areas up to a quarter of a 2'' wafer on *InP* (100), ranging from the tuning of the growth conditions to the substrate preparation. While this study focuses on *InP* substrate, we believe the lessons learned can be relevant to other substrates. In particular, we highlight the long time necessary to completely desorb the native substrate oxide, key to obtain monocrystalline layers. We also provide the temperature and II/V flux window that lead to stoichiometric and crystalline growth. Finally, we compare the luminescence between monocrystalline and polycrystalline layers. Luminescence from polycrystalline samples is dominated by emission below the bandgap. Monocrystalline samples also exhibit luminescence below the bandgap. Compared to the polycrystalline, the emission is considerably brighter and at lower energy. In addition, we observe band-edge

luminescence, a sign of the high quality of the material. Further work is needed to identify the physical origin of the luminescence bands below the bandgap.

Methods

Zn_3P_2 thin films were grown using a Veeco GENxplor MBE system operating with separate *Zn* and *P* sources. The samples are obtained on *InP*(100) substrate. Substrate preparation includes two steps of degassing for two hours at $150^\circ C$ and $300^\circ C$ and a third stage at $580^\circ C$ under P_2 equivalent beam pressures $> 1 \times 10^{-6} Torr$. Unless otherwise stated, the duration of this step is 10 mins.

All the Raman measurements reported in Figure 1 are done using confocal micro-Raman spectroscopy operating with a 532 nm laser. The spectra offered is accumulation of 20

counts, each having the exposure time of **1s** and laser power of **9 μ W**.

The micro-Raman measurements shown in Figure 2 have been acquired in back-scattering geometry at 12 K using the 532 nm line of a Coherent Sapphire SF laser for excitation. A microscope objective with a numerical aperture of 0.75 was used to focus the light onto the sample to a spot with a diameter of about **1 μ m**. The incident light is linearly polarized, while all the scattered light is collected regardless of the polarization. The signal was analysed using a TriVista triple spectrometer with 900, 900 and 1800 mm^{-1} gratings in subtractive mode and a Princeton Instruments multichannel CCD PyLoN camera. The SEM images in Figure 1 and Figure 2 are acquired in a Zeiss Merlin field emission microscope. The TEM samples in Figure 3 are prepared by Zeiss NVision 40 CrossBeam dual focused ion beam (FIB)/ SEM with liquid Ga ion source. TEM images in Figure 3 are captured by FEI Tecnai Osiris operating at **200 KeV**. The STEM images and EELS maps in Figure 3 are captured by a FEI Titan Themis 60-300 kV, equipped with X-FEG, monochromator, C_s aberration (image and probe) correctors, and Gatan GIF Quantum ERS spectrometer, operating at **200 KeV**.

The XRD patterns in Figure 4 are captured by a Panalytical Empyrean diffractometer operating in Goni scan configuration with a Cu (K- α) X-ray source of 1.54 Å operating at **45 KeV** and **40mA**.

The micro-photoluminescence measurements, shown in figure 5, have been acquired in back-scattering geometry at 20 K using the 488 nm line of a Coherent Sapphire SF laser and an Andor iDus DV420A-OE detector. The spectra have been corrected for the response of the detector. A microscope objective with a numerical aperture of 0.75 was used to focus the light onto the sample to a spot with a diameter of about **1 μ m**. Radiant fluxes of approximately **470 μ W**, **470 μ W**, **0.47 μ W** and **1170 μ W** were used on the monocrystalline, polycrystalline 1, polycrystalline 2 and InP substrate samples, respectively. 100 accumulations of 1s, **~0.01s** and **~0.01s** were used on the first three samples, respectively, and 1 accumulation of **~0.01s** was used to acquire the spectrum from **InP**.

References

- Wadia C, Alivisatos AP, Kammen DM. Materials availability expands the opportunity for large-scale photovoltaics deployment. *Environ Sci Technol* [Internet]. 2009 Mar 15 [cited 2020 Jul 27];43(6):2072–7. Available from: <https://pubs.acs.org/sharingguidelines>
- Zhang X, Huang M, Xu P, Dai CM, Cai ZH, Han D, et al. Earth-abundant photovoltaic semiconductor NaSbS₂ in the rocksalt-derived structure: A first-principles study. *Prog Nat Sci Mater Int*. 2019 Jun 1;29(3):322–8.
- Adachi S. Earth-Abundant Materials for Solar Cells: Cu₂-II-IV-VI₄ Semiconductors [Internet]. Wiley; 2015 [cited 2020 Jul 27]. Available from: <https://onlinelibrary.wiley.com/doi/book/10.1002/9781119052814>
- Hall RB, Birkmire RW, Phillips JE, Meakin JD. Thin-film polycrystalline Cu₂S/Cd_{1-x}Zn_xS solar cells of 10% efficiency. *Appl Phys Lett*. 1981;38(1!).
- Wadia C, Wu Y, Gul S, Volkman SK, Guo J, Alivisatos AP. Surfactant-assisted hydrothermal synthesis of single phase pyrite FeS₂ nanocrystals. *Chem Mater* [Internet]. 2009 Jul 14;21(13):2568–70. Available from: <http://pubs.acs.org>.
- Yuan B, Luan W, Tu ST, Wu J. One-step synthesis of pure pyrite FeS₂ with different morphologies in water. *New J Chem* [Internet]. 2015 May 1;39(5):3571–7. Available from: www.rsc.org/njc
- Yin L, Cheng G, Feng Y, Li Z, Yang C, Xiao X. Limitation factors for the performance of kesterite Cu₂ZnSnS₄ thin film solar cells studied by defect characterization. *RSC Adv* [Internet]. 2015 Apr 30;5(50):40369–74. Available from: www.rsc.org/advances
- S. P, P. T. Thin Film Solar Cells Using Earth-Abundant Materials. In: *Solar Cells - Research and Application Perspectives* [Internet]. InTech; 2013. Available from: <http://dx.doi.org/10.5772/51734>
- Seragg JJ, Dale PJ, Colombara D, Peter LM. Thermodynamic aspects of the synthesis of thin-film materials for solar cells. *ChemPhysChem* [Internet]. 2012 Aug 27;13(12):3035–46. Available from: <https://chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/cphc.201200067>
- Liu Y, Zhou B, Lv W, Wu C, Su X, Wang J. Experimental investigation and thermodynamic assessment of the Zn–Si–P system. *Surf Coatings Technol*. 2016 Nov 25;306:370–7.
- Tu H, Yin F, Su X, Liu Y, Wang X. Experimental investigation and thermodynamic modeling of the Al–P–Zn ternary system. *Calphad Comput Coupling Phase Diagrams Thermochem*. 2009 Dec 1;33(4):755–60.
- Ghasemi M, Stutz E, Escobar Steinvall S, Zamani M, Fontcuberta i Morral A. Thermodynamic re-assessment of the Zn–P binary system. *Materialia*. 2019 Jun 1;6:100301.
- Swinkels MY, Campo A, Vakulov D, Kim W, Gagliano L, Steinvall SE, et al. Measuring the Optical Absorption of Single Nanowires. *Phys Rev Appl*. 2020 Aug 1;14(2):024045.
- Fagen EA. Optical properties of Zn₃P₂. *J Appl Phys*. 1979 Oct 25;50(10):6505–15.
- Kimball GM, Müller AM, Lewis NS, Atwater HA. Photoluminescence-based measurements of the energy gap and diffusion length of Zn₃P₂. *Appl Phys Lett* [Internet]. 2009 Sep 14;95(11):112103. Available from:

- <http://aip.scitation.org/doi/10.1063/1.3225151>
16. Wyeth NC, Catalano A. Spectral response measurements of minority-carrier diffusion length in Zn₃P₂. *J Appl Phys* [Internet]. 1979 Mar 29;50(3):1403–7. Available from: <http://aip.scitation.org/doi/10.1063/1.326122>
 17. Pseudomorphic growth and strain relaxation of α -Zn₃P₂ on GaAs(001) by molecular beam epitaxy. *J Cryst Growth* [Internet]. 2013 Jan 15;363:205–10. Available from: <http://www.sciencedirect.com/science/article/pii/S0022024812007695>
 18. Sierański K, Szatkowski J, Misiewicz J. Semiempirical tight-binding band structure of II3V2 semiconductors: Cd₃P₂, Zn₃P₂, Cd₃As₂, and Zn₃As₂. *Phys Rev B* [Internet]. 1994 Sep 15 [cited 2020 Jul 27];50(11):7331–7. Available from: <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.50.7331>
 19. Stackelberg, M.V, Paulus P. Investigation of Phosphides and Arsenides of Zinc and Cadmium, The Structure of Zn₃P₂,. *phys Chem*. 1935;427–760.
 20. Suda T, Kakishita K, Sato H, Sasaki K. N-type zinc phosphide grown by molecular beam epitaxy. *Appl Phys Lett* [Internet]. 1996 Jun 4 [cited 2017 Oct 4]; Available from: <http://aip.scitation.org/doi/10.1063/1.117659>
 21. Long J. The Growth of Zn₃P₂ by Metalorganic Chemical Vapor Deposition. *J Electrochem Soc*. 1983;130(3):725.
 22. Chu TL, Chu SS, Murthy K, Stokes ED, Russell PE. Deposition and properties of zinc phosphide films. *J Appl Phys*. 1983 Apr 14;54(4):2063–8.
 23. Escobar Steinvall S, Tappy N, Ghasemi M, Zamani RR, Lagrange T, Stutz EZ, et al. Multiple morphologies and functionality of nanowires made from earth-abundant zinc phosphide. *Nanoscale Horizons*. 2020 Feb 1;5(2):274–82.
 24. Escobar Steinvall S, Ghisalberti L, Zamani RR, Tappy N, Hage FS, Stutz EZ, et al. Heterotwin Zn₃P₂ superlattice nanowires: the role of indium insertion in the superlattice formation mechanism and their optical properties. *Nanoscale*. 2020 Nov 20;12(44):22534.
 25. Escobar Steinvall S, Stutz EZ, Paul R, Zamani M, Dzade NY, Piazza V, et al. Towards defect-free thin films of the earth-abundant absorber zinc phosphide by nanopatterning. *Nanoscale Adv*. 2021;3:326–32.
 26. Paul R, Humblot N, Humblot N, Steinvall SE, Stutz EZ, Joglekar SS, et al. Van der Waals Epitaxy of Earth-Abundant Zn₃P₂ on Graphene for Photovoltaics. *Cryst Growth Des* [Internet]. 2020 Jun 3 [cited 2020 Aug 3];20(6):3816–25. Available from: <https://dx.doi.org/10.1021/acs.cgd.0c00125>
 27. Stutz EZ, Escobar Steinvall S, Litvinchuk AP, Leran J-B, Zamani M, Paul R, et al. Raman spectroscopy and lattice dynamics calculations of tetragonally-structured single crystal zinc phosphide (Zn₃P₂) nanowires. *Nanotechnology* [Internet]. 2021 Feb 19 [cited 2020 Dec 7];32(8):085704. Available from: <https://iopscience.iop.org/article/10.1088/1361-6528/abc91b>
 28. Grillo V, Carlino E, Glas F. Influence of the static atomic displacement on atomic resolution Z-contrast imaging. *Phys Rev B - Condens Matter Mater Phys*. 2008 Feb 11;77(5):054103.
 29. De La Mata M, Magen C, Gazquez J, Utama MIB, Heiss M, Lopatin S, et al. Polarity assignment in ZnTe, GaAs, ZnO, and GaN-AlN nanowires from direct dumbbell analysis. *Nano Lett*. 2012 May 9;12(5):2579–86.
 30. Zamani RR, Gorji Ghalamestani S, Niu J, Sköld N, Dick KA. Polarity and growth directions in Sn-seeded GaSb nanowires. *Nanoscale*. 2017 Mar 7;9(9):3159–68.
 31. PDF 00-032-0452 [Internet]. [cited 2020 Nov 13]. Available from: <https://www.icdd.com/pdfsearch/>
 32. PDF 00-053-0591 [Internet]. [cited 2020 Nov 13]. Available from: <https://www.icdd.com/pdfsearch/>
 33. Stamov IG, Syrbu NN, Dorogan A V. Energetic band structure of Zn₃P₂ crystals. *Phys B Condens Matter*. 2013 Jan;408(1):29–33.
 34. Yamazaki M, Nakagawa M, Jimbo K, Shimamune Y, Katagiri H. Photoluminescence study of Cu₂ZnSnS₄ thin film solar cells. *Phys Status Solidi Curr Top Solid State Phys* [Internet]. 2017 Jun 1 [cited 2020 Dec 3];14(6). Available from: <https://onlinelibrary.wiley.com/doi/full/10.1002/pssc.201600202>
 35. Halliday DP, Potter MDG, Mullins JT, Brinkman AW. Photoluminescence study of a bulk vapour grown CdTe crystal. *J Cryst Growth*. 2000 Nov 15;220(1–2):30–8.
 36. Briones F, Wang FC, Bube RH. Pair transitions in Zn₃P₂. *Appl Phys Lett*. 1981 Nov 15;39(10):805–7.